Dielectric function and magneto-optical Voigt constant of Cu₂O: A combined spectroscopic ellipsometry and polar magneto-optical Kerr spectroscopy study

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Cuprous oxide is a highly interesting material for the emerging field of transparent oxide electronics. In this work the energy dispersion of the dielectric function of Cu_2O bulk material is revised by spectroscopic ellipsometry measurements in an extended spectral range from 0.73 to 10 eV. For the first time, the magneto-optical Kerr effect was measured in the spectral range from 1.7 to 5.5 eV and the magneto-optical Voigt constant of Cu_2O was obtained by numerical calculations from the magneto-optical Kerr effect spectra and the dielectric function.

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I. INTRODUCTION

Cuprous oxide (Cu₂O) is a *p*-type semiconductor due to copper vacancies¹ or oxygen interstitials,² with reported values of the band gap between 2 and 2.4 eV (see Table I). Cu₂O can be found as a natural crystal, named cuprite, or can be produced by oxidizing copper at high temperatures.^{3,4}

Cu₂O was intensively investigated in the past as a possible candidate for inexpensive solar cell fabrication.^{1,5} Even though the theoretical limit of the power conversion efficiency for Cu₂O based solar cells is about 18%,⁶ the highest efficiency achieved was 2%.⁷ More recently, transparent conducting oxide (TCO)/Cu₂O heterojunction solar cells, such as ZnO/Cu₂O have also been investigated.⁸ However, efforts are still needed to improve the film characteristics, in particular the minority carrier transport length.⁹ On the other hand, Cu₂O was already used as injection material in metal-based transistors¹⁰ going into the direction of spin injection and as base material for diluted ferromagnetic semiconductors.¹¹

Even though Cu₂O is known for decades, there are still divergent reports regarding its electronic and optical properties. Early optical measurements in a broad spectral range were reported by Brahms *et al.* (spectral range of 2.5 to 6.5 eV),¹² Balkanski *et al.* (2–6 eV),¹³ and Tandon *et al.* (1.24–6.2 eV).¹⁴ Spectroscopic ellipsometry (SE) measurements performed by Ito *et al.*¹⁵ revealed well-separated features in the dielectric function. In the modeling of the ellipsometric data, Ito *et al.* used Lorentzian oscillators, while surface roughness (SR) was not considered.¹⁵ Due to their large tales, the use of Lorentzian peaks results in an absorption-like behavior even in the red and near-infrared (IR) range, in contradiction to the obvious transparency of cuprite in the red region of the electromagnetic spectrum.

Cu₂O also received significant attention from a theoretical point of view. A detailed calculation of the electronic energy bands was reported by Dahl *et al.*,¹⁶ who obtained a direct band gap of 1.77 eV, thus slightly underestimating the ones obtained experimentally. However, modern density functional theory (DFT) calculations underestimate the band gap much more (0.5–0.8 eV, see Ref. 17 and references therein), while Hartree-Fock methods overestimate significantly the band gap (9.7 eV¹⁸). Table I provides a survey of the band-gap values obtained by different calculation methods.

The electronic structure was intensively studied by Ghijsen *et al.* with photoemission (PES) and inverse photoemission (IPES) measurements.¹⁹ More recent angular resolved PES (ARPES) measurements were compared with theoretical data of the Cu₂O band structure obtained using scGW²⁰ and LDA + U²¹ methods. Even though progress has been made regarding the agreement between the theoretically and experimentally determined band structures, there still are some discrepancies between the measured and the calculated density of states.²¹

The scope of the present work is to extend the spectral range of known optical constants and to improve their accuracy in the spectral range already reported in previous studies. In addition, we report for the first time the magneto-optical material parameter Q, the so-called Voigt constant, in the near-IR to near-ultraviolet (UV) spectral range as a further support for future theoretical interpretation of the optical spectrum. For this purpose, we exploit the magneto-optical Kerr effect (MOKE) in polar geometry, which describes the change in the polarization state of light induced by reflection on a sample exposed to a magnetic field oriented perpendicular to the sample plane. Its origin lies in the modification of the dielectric properties of the material in the presence of a magnetic field. The effect can be described by the occurrence of Q in the off-diagonal components of the macroscopic dielectric tensor. In the polar MOKE geometry, as used in this work, the light propagates along the z direction and hence parallel to the magnetic field direction. Since Cu₂O is an optically isotropic material, the dielectric tensor has the following form:

$$\underline{\varepsilon} = \varepsilon \begin{pmatrix} 1 & i Q & 0 \\ -i Q & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

While spectroscopic ellipsometry is commonly used to determine the optical constants of materials, generalized magneto-optical spectroscopic ellipsometry (see, e.g., Ref. 28) or MOKE spectroscopy in combination with SE (see, e.g., Ref. 29) is applied to obtain the off-diagonal dielectric tensor elements of oxides.

The knowledge of the magneto-optical activity of the pure Cu_2O is needed when characterizing advanced heterostructures of Cu_2O /diluted ferromagnetic semiconductors

TABLE I. Literature values for the band gap of Cu_2O determined by different measurement techniques and calculation methods. The abbreviations APW, OLCAO, H-F, FP-LAPW and PBE + GGA stand for Augmented Plane Wave, Orthogonalized Linear Combination of Atomic Orbitals, Hartree-Fock, Full Potential Linearized Augmented Plane Wave, Perdew-Burke-Ernzerhof + Generalized Gradient Approximation, respectively.

Band gap (eV)	Measurement technique	Ref.	Band gap (eV)	Calculation method	Ref.
2.02	Diffuse reflectance	14	1.77	APW	16
2.17	Absorption	22	0.78	OLCAO	25
2.2	Reflectance and transmittance	23	9.7	Periodic H-F	18
2.17	Transmission	24	~ 0.5	FP-LAPW	26
2.4 ± 0.3	PES + IPES	19	0.54-1.97	Different approaches	20
			0.53-2.36	Different approaches	27
			0.7	PBE + GGA	17

or $Cu_2O/magnetic TCO$ by magneto-optical means. This paper presents Kerr rotation and ellipticity data in the spectral range between 1.7 and 5.5 eV. From these, the Voigt constant is derived in a Kramers-Kronig (KK) consistent way, allowing the prediction of MOKE, Faraday, or magnetic circular dichroism (MCD) spectra of layer systems containing Cu_2O .

II. EXPERIMENT

The investigated cuprite (Cu_2O) natural single crystal, with (100) surface orientation, one side polished, and having a thickness of 1 mm, was purchased from SurfaceNet GmbH. The crystal is translucent with a red color.

Ellipsometric measurements were performed with two instruments: a commercial Variable Angle Spectroscopic Ellipsometer (VASE, J. A. Woollam Co. Inc.) and a Vacuum UltraViolet (VUV) ellipsometer,³⁰ using synchrotron light as a source at BESSY II, Berlin. The VASE data were recorded from 0.73 to 4.99 eV photon energy with a 0.02 eV step at different incidence angles (65, 70, and 75°). The VUV measurements were performed in the energy range from 4 to 10 eV with a step of 0.025 eV at the fixed angle of incidence (67.5 \pm 0.5°).

The magneto-optical characterization was performed using a home-built MOKE spectrometer using the reflection anisotropy configuration³¹ in the energy range from 1.7 to 5.5 eV. The extension for MOKE measurements is realized using an electromagnet that can apply a magnetic field perpendicular to the sample surface (polar geometry).³² The setup measures the tilt $\theta_{\rm K}$ and ellipticity $\eta_{\rm K}$ of the polarization of the light reflected from the sample surface exposed to a magnetic field of 1.7 T.

The magnetic moment of the Cu_2O sample was investigated using superconducting quantum interference device (SQUID; QD MPMS XL) magnetometry.

III. RESULTS AND DISCUSSIONS

A. Ellipsometry

The optical response of cuprite was determined in the spectral range from 0.73 to 10 eV by overlapping the data measured with the VASE and VUV ellipsometers in an energy region between 4 and 5 eV.

The effective dielectric function was determined using the WVASE32[®] (J. A. Woollam Company) analysis software and is plotted in Fig. 1 as dashed black line. For ideal samples, the effective dielectric function, defined as the dielectric function

of a virtually semi-infinite layer with a smooth surface,³³ coincides with the true dielectric function of the material. The line shape of $\langle \varepsilon_2 \rangle$ in Fig. 1 is similar to that of the dielectric function determined by Ito *et al.*¹⁵ However, a significant absorption tail well below 2.0 eV is noticeable. This cannot be real since, by bare eye, it can be seen that the crystal with a thickness of ~1 mm is transparent for red visible light. Ito *et al.* also state that cuprite has a "reddish" color.¹⁵ Therefore, in a second step, a more sophisticated model was used to model the experimental data, i.e., by introducing SR. SR leads to light scattering at the sample surface, which, in turn, reduces the polarization degree of the reflected light beam. Depolarization effects and scattering may thus appear as absorption in the calculated dielectric function, when the SR is neglected.

It is commonly accepted that semiconductor materials can be well described in the transparent range by a Cauchy dispersion layer, see, e.g., Ref. 34. We modeled the data in the energy range (0.7–2.1 eV) using an optical three-layer model that consists of a semi-infinite Cauchy layer (as substrate), a SR layer on top, and air. The SR was modeled as a layer consisting of a mixture of 50% material (having the same optical constants as the semi-infinite Cauchy layer) and 50% void using the



FIG. 1. (Color online) The real $(\langle \varepsilon_1 \rangle)$ and imaginary $(\langle \varepsilon_2 \rangle)$ part of the effective dielectric function of cuprite (dashed black lines) determined assuming a single Cu₂O semi-infinite layer (upper inset). The real (ε_1) and imaginary (ε_2) part of the dielectric function of cuprite (full red lines) determined using a point-by-point fit, assuming a single Cu₂O semi-infinite layer covered with a layer simulating the SR (lower inset).



FIG. 2. (Color online) Example of AFM image of the Cu₂O crystal surface. The average rms roughness of all scans performed was determined to be 4.8 ± 0.4 nm.

effective medium approximation (EMA) algorithm based on the Bruggeman equation,³⁵ which is implemented in the WVASE32 code. The calculated ellipsometric parameters Ψ and Δ were fitted to the experimental ones, with the free parameters of the fit being the Cauchy dispersion parameters and the SR layer thickness. The upper boundary of 2.1 eV of the energy range of the fit was chosen slightly below the parity forbidden direct band gap of Cu_2O of 2.17 eV³⁶ to avoid any absorption effects of higher order. The best match to the measured ellipsometric data, judging from the mean square error values and the optical inspection of the fit to experimental Ψ and Δ curves, was obtained for a SR layer thickness of (11.0 \pm 1.0) nm. This value agrees well with the results of atomic force microscopy (AFM) measurements, if one considers the thickness of the roughness layer to be double of the root mean square roughness $(2 \times \text{rms} = (9.6 \pm 0.8) \text{ nm})$ of the scans, i.e., the double of the average plus/minus deviation from an average level. An example scan image is shown in Fig. 2.

Afterwards a point-by-point fit of the ellipsometric parameters Ψ and Δ in the whole spectral range (0.7 to 10) eV was performed to obtain the dielectric function of



FIG. 3. Dielectric function of Cu_2O determined by a point-bypoint fit (circles) and the fitted curve using Gaussian peaks (full line). The parameters of individual peaks (dashed lines, assigned by grey numbers) are given in Table II.

the substrate. The SR layer thickness was kept fixed (11 nm) during the point-by-point fit. A schematic drawing of the model is presented in the inset of Fig. 1. The resulting dielectric function is presented in Fig. 1 by a full red line. The noise is caused by the low light intensity of the VASE setup between 4.5 and 5 eV. Besides SR also the formation of other species on the surface, like CuO or Cu(OH)₂,³⁷ could influence the optical response in a similar manner. It is, however, difficult to distinguish their contribution from that of SR.

The absorption onset resulting from our modeling with SR lies slightly below 2.5 eV. This corresponds to the optical transition from the valence band into the second conduction band (energy difference of 2.65 eV) considering the rather large exciton energies in Cu₂O of more than 0.1 eV.³⁶ The direct band gap of 2.17 eV is, as mentioned, parity forbidden. Therefore, its contribution to absorption is so small that it can be neglected in the ellipsometry data evaluation.

The dielectric function was then fitted with Gaussian peaks in ε_2 to determine the position of the spectral features. The real part ε_1 is calculated KK consistently from ε_2 (see, e.g., Ref. 38). In Fig. 3 the real (ε_1) and imaginary parts (ε_2) of the dielectric function (empty circles) and the deconvolution using

TABLE II. Parameters of the Gaussian peaks used to model the imaginary part of the dielectric function. Peak 3 was used for better fit, although it does not present any well-defined feature in the spectra. Corresponding energy positions reported previously in literature are given in columns 5 to 7.

Peak	Energy (eV)	Amplitude (a.u.)	Broadening (eV)	Energy (eV) ¹⁵	Energy (eV) ¹²	Energy (eV) ¹⁴
1	2.60 ± 0.02	1.78 ± 0.05	0.053 ± 0.020	2.64	2.61	
2	2.72 ± 0.02	3.32 ± 0.05	0.112 ± 0.020	2.76	2.71	2.67
3	2.87 ± 0.02	3.83 ± 0.05	0.334 ± 0.020			
4	3.48 ± 0.02	13.76 ± 0.05	0.773 ± 0.020	3.45	3.62	3.85
5	4.18 ± 0.02	9.63 ± 0.05	0.457 ± 0.020	4.25	4.33	
6	4.62 ± 0.02	7.13 ± 0.05	0.649 ± 0.020		4.48; 4.74; 4.86	4.64
7	5.21 ± 0.02	4.76 ± 0.05	0.546 ± 0.020		5.36	5.00
8	6.33 ± 0.02	1.16 ± 0.05	0.885 ± 0.020		6.45	
9	7.31 ± 0.02	0.52 ± 0.05	0.910 ± 0.020			
10	9.68 ± 0.02	1.88 ± 0.05	1.190 ± 0.020			

Gaussian peaks (full lines) are shown. The energy position, the amplitude, and the broadening of the Gaussian peaks are given in Table II.

As mentioned above, the fit with Gaussian peaks serves for the identification of the position of spectral features. Obviously, it would be more reasonable in the case of a crystalline semiconductor like Cu_2O to start off with a parabolic band model and subsequently extend it to a fully parametrized semiconductor model taking into account the band structure. However, a data fit with such a model is not possible from the experimental data alone, because of too many unknown parameters involved.

B. Magneto-optical Kerr effect spectroscopy

The experimental MOKE spectrum of the Cu_2O crystal is presented in Fig. 4.

The Kerr rotation of about 0.1 mrad observed for Cu₂O crystal lies in the same order as that observed for molecular films.³⁹ In order to check the origin of the MOKE signal, the Cu₂O crystal was measured in a SQUID magnetometer at room temperature (which corresponds to the temperature of the MOKE experiments). To ensure a good sensitivity to small amount of magnetic species present in the sample the measurements were performed in an applied magnetic field of 6 T, i.e., by a factor of 3.5 larger than the applied field in the MOKE experiment. The signal obtained after diamagnetic correction exhibits neither paramagnetic contribution nor a hysteresis loop within the detection limits as visible in Fig. 5. This confirms that the Cu₂O crystal under study is purely diamagnetic and if any magnetic impurities are present, their magnetic response is negligible. Thus the magnetooptical signal observed by MOKE spectroscopy is an intrinsic property of the crystal.

From the MOKE spectra together with the optical constants obtained by spectroscopic ellipsometry, the material Voigt constant Q can be determined as a free parameter by a point-by-point fitting procedure.⁴⁰ The result is shown in Fig. 6



FIG. 4. (Color online) Experimental MOKE spectrum of Cu_2O (thin lines with symbols) and modeled using the KK-consistent Voigt constant Q (thick solid lines) and the dielectric function obtained by point-by-point fitting.



FIG. 5. (Color online) M-H curve of the Cu₂O crystal at 300 K obtained from SQUID magnetometry. The sample is found to be fully diamagnetic within the experimental sensitivity.

as thin line with symbols. Subsequently, the dispersion of the Voigt constant is modeled by a sum of KK-consistent Gaussian functions³⁸ and their derivatives. This procedure is conducted following the Faraday term formalism described by Stephens.⁴¹ Stephens used the shape of absorption features for describing Faraday A terms and the derivative for B and C terms in the energy dispersion of magnetic circular dichroism (MCD). We adopt a similar procedure: as the typical line shape of features in the imaginary part ε_2 of the diagonal elements of the dielectric tensor is well described by Gaussian functions, we use Gaussian functions as well as derivative-like-shaped features to calculate the Voigt constant spectrum of Cu₂O. The KK-consistent Gaussian function can



FIG. 6. (Color online) Energy dispersion of the Cu_2O Voigt constant modeled point-by-point from the MOKE data and the dielectric function (thin lines with symbols) compared to the Voigt constant modeled using KK-consistent functions (thick solid line; see Table III and Fig. 7)

be written as³⁸

$$\operatorname{Re} g_{\mathrm{KK}} = \frac{2A}{\sqrt{\pi}} \left(D\left(2\sqrt{\ln 2}\frac{E+E_0}{FWHM}\right) - D\left(2\sqrt{\ln 2}\frac{E-E_0}{FWHM}\right) \right)$$
$$\operatorname{Im} g_{\mathrm{KK}} = A\left(\exp\left(-4\ln 2\left(\frac{E-E_0}{FWHM}\right)^2\right) - \exp\left(-4\ln 2\left(\frac{E+E_0}{FWHM}\right)^2\right) \right),$$

with A being the amplitude, E_0 the energy position, and FWHM the full width at half maximum value. D is the Dawson function, which can be calculated numerically. It is defined as

$$\mathbf{D}(x) = \exp(-x^2) \int_0^x \exp(t^2) dt.$$

The derivative of the Gaussian function is given by (under preservation of the odd symmetry around E = 0 eV, which accounts for time inversion invariance, taken into account by sign change at the negative energy half axis):

$$\operatorname{Re}\frac{dg}{dE} = \frac{4\sqrt{\ln 2}}{FWHM\sqrt{\pi}} \left(\left(1 - \frac{4\sqrt{\ln 2}}{FWHM} (E + E_0) D\left(2\sqrt{\ln 2} \frac{E + E_0}{FWHM} \right) \right) + \left(1 - \frac{4\sqrt{\ln 2}}{FWHM} (E - E_0) D\left(2\sqrt{\ln 2} \frac{E - E_0}{FWHM} \right) \right) \right)$$
$$\operatorname{Im}\frac{dg}{dE} = \frac{8\ln 2}{FWHM^2} \left((E - E_0) \exp\left(-4\ln 2\left(\frac{E - E_0}{FWHM}\right)^2 \right) + (E + E_0) \exp\left(-4\ln 2\left(\frac{E + E_0}{FWHM}\right)^2 \right) \right).$$

The function parameters used in the present model are summarized in Table III. The deconvolution is presented in Fig. 7. The Gaussian peak 4, which is outside the spectral range measured by MOKE, is needed in the real part of Q and plays the role of a pole. Therefore its height and broadening are strongly correlated and its parameters are governed by a large uncertainty.

The use of the Gaussian functions alone already yields a reasonable agreement between the experimental MOKE data and the model fit. The positions of the Gaussian peaks can be identified with maxima in the imaginary part of ε . This can also be seen by the comparison of the Tables II and III. The peaks in ε_2 at 3.48, 4.18, and 5.21 eV correspond quite reasonably to the ones in Q at 3.50, 4.30, and 5.21 eV. These features can therefore be attributed to Faraday B or C terms,^{41,42} although the broadening does not agree that well between ε_2 and Q features. This discrepancy could be caused by the use of Gaussian peaks as an approximation for the true B-term line shape. B-term transitions have a nondegenerated ground state and a set of excited states, which are close to degeneracy, e.g., they would be degenerated in the next higher symmetry group. B terms therefore usually appear in pairs with the component peaks close in energy but with different signs. This situation is not found in the present data. C terms arise from a degeneracy in the ground state, which is lifted in the presence of a magnetic field. The difference in the occupancy of the new "ground states" due to Boltzmann statistics is directly related to the oscillator strength of the C-term feature in MCD or Q, respectively. Consequently, these features are temperature dependent. At T = 0 K a C-term feature has its largest amplitude because the difference in occupancy of the ground and excited energy levels is maximum. For $T \rightarrow \infty$, a C-term feature does not completely vanish but transforms into a derivative-like line shape (similar to an A term). An A-term arises from an optical transition between a nondegenerated ground state and a degenerated excited state, the degeneracy of which is lifted in a magnetic field. From measurements performed at room temperature, it is often not possible to distinguish between an A and a C term. The Gaussian features in the present data are probably C terms because they do not appear in pairs with opposite signs. However, in order to unambiguously confirm this assignment, temperature-dependent measurements are planned. Care must also be taken because at the basis of the Faraday term formalism lies the assumption that the degenerated energy levels involved in the magneto-optical transitions undergo the normal Zeeman effect. This assumption applies well to atomic or molecular spectra,⁴² which correspond to transitions

TABLE III. Model function types and parameters of the Q dispersion.

Peak	Туре	Energy position (eV)	Amplitude (a.u.)	Broadening (eV)
1	Gaussian derivative (1)	2.575 ± 0.010	$-(1.86 \pm 0.20) \times 10^{-6}$	0.080 ± 0.010
2	Gaussian derivative (2)	2.655 ± 0.010	$(1.92 \pm 0.20) \times 10^{-6}$	0.075 ± 0.010
3	Gaussian (1)	3.498 ± 0.020	$(4.933 \pm 0.020) \times 10^{-5}$	0.524 ± 0.020
4	Gaussian (2)	4.301 ± 0.020	$(2.394 \pm 0.002) \times 10^{-4}$	0.696 ± 0.020
5	Gaussian (3)	5.208 ± 0.020	$(2.291 \pm 0.020) \times 10^{-5}$	0.391 ± 0.020
6	Gaussian (4)	6.29 ± 0.10	$-(1.152 \pm 0.010) \times 10^{-3}$	0.34 ± 0.10



FIG. 7. Deconvolution of the Voigt constant dispersion of Cu_2O . The parameters are given in Table III.

between discrete energy levels. The present empirical trial to adopt this formalism for a bulk semiconductor, Cu_2O , which is characterized by energy bands, appears to be successful regarding the agreement between fit and experimental data. However, for an accurate description of the line shape of the features, a band structure model would certainly be of great help.

In the dielectric function, two sharp features appear at around 2.6 eV. At the corresponding position in the MOKE spectra, very weak features, not much higher than the noise level, can also be observed. The best agreement between experiment and calculated curve in this spectral range was obtained when using two Gaussian derivatives (A terms) with opposite signs. A description with Gaussian functions would require at least one additional peak, which would have no correspondent structure in ε_2 . The presence of A terms suggests a nondegenerated ground state and a degenerated excited state for these sharp features. This line shape is consistent with the excitonic character of these two optical transitions, since the excited electronic states are accompanied by excitonic sublevels.

IV. CONCLUSIONS

The dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of Cu₂O single crystal at room temperature was obtained by spectroscopic ellipsometry in the spectral range from 0.73 to 10.00 eV. This improves the present knowledge of ε over the photon energy compared to previous reports (1.2 to 5.2 eV).¹⁵ The model used for the numerical evaluation of the experimental data takes into account a small SR, which accounts for the obvious transparency of Cu₂O in the visible red spectral range and yields higher ε_2 values in the energy range between 3.1 and 5.5 eV.

In addition, the magneto-optical Voigt constant, which describes the influence of an external magnetic field on the off-diagonal elements of the dielectric tensor, was determined in the energy range between 1.7 and 5.5 eV at a magnetic field of 1.7 T. The Voigt constant was determined numerically, using an optical layer model, from the experimental MOKE spectrum and the dielectric function, and then a KK-consistent fit of its line-shape was obtained.

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